

Development of a Kohn-Sham like potential in the Self-Consistent Atomic Deformation Model

M. J. Mehl, L. L. Boyer and H. T. Stokes
Complex Systems Theory Branch
Naval Research Laboratory
Washington, D.C. 20375-5345

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Abstract

This is a brief description of how to derive the local “atomic” potentials from the Self-Consistent Atomic Deformation (SCAD) model density function. Particular attention is paid to the spherically averaged case.

1 The SCAD Model

The Self-Consistent Atomic Deformation (SCAD) model [1] has been described as an extension of the work of Gordon and Kim [2]. It can also be viewed as an approximation to density functional theory, which is the point of view taken in this paper.

The SCAD model approximates the exact electronic density functional [3] by the form:

$$E[n(\mathbf{r})] = \sum_i T_0[n_i(\mathbf{r})] + \left\{ T_{TF}[n(\mathbf{r})] - \sum_i T_{TF}[n_i(\mathbf{r})] \right\} + F[n(\mathbf{r})] . \quad (1)$$

Here:

1. $T_0[n_i(\mathbf{r})]$ is the kinetic energy of non-interacting electrons centered about the site \mathbf{R}_i ,

$$T_0[n_i(\mathbf{r})] = - \sum_{\alpha} \int \psi_{i\alpha}^*(\mathbf{r}) \nabla^2 \psi_{i\alpha}(\mathbf{r}) d^3r , \quad (2)$$

where the $\psi_{i\alpha}$ are an orthonormal set of wave functions such that

$$n_i(\mathbf{r}) = \sum_{\alpha} |\psi_{i\alpha}(\mathbf{r})|^2 . \quad (3)$$

(We use atomic units, with $\hbar = 2m = e^2/2 = 1$, where m is the mass of the electron and $-e$ is its charge.)

2. We assume that the charge associated with each site,

$$N_i = \int n_i(\mathbf{r}) d^3r , \quad (4)$$

is fixed. That is, there is no charge transfer between sites during the iteration of the problem to self-consistency.

3. The total density of the system is given by

$$n(\mathbf{r}) = \sum_i n_i(\mathbf{r} + \mathbf{R}_i) . \quad (5)$$

4. The Thomas-Fermi kinetic energy is given (in Rydberg units) by

$$T_{TF}[n(\mathbf{r})] = \frac{3}{5}(3\pi^2)^{\frac{2}{3}} \int n^{\frac{5}{3}}(\mathbf{r}) d^3r . \quad (6)$$

The sum over atomic Thomas-Fermi kinetic energies in (1) is to cancel this contribution to $E[n]$ from the individual atoms, where the kinetic energy is given by (2). The Thomas-Fermi terms in parenthesis in (1) thus represent the overlap kinetic energy, and vanish when the atoms are separated by large distances.

5. The functional $F[n(\mathbf{r})]$ contains the remaining density functional terms[3, 4], including the Coulomb interaction terms (electron-electron, electron-nucleus, and nucleus-nucleus), which is a simple functional of the total density (5), and the exchange-correlation term, which is local functional of the density within the Local Density Approximation (LDA). The functional derivative of F with respect to the total density is just the Kohn-Sham potential [4],

$$v_{KS}[n(\mathbf{r}); \mathbf{r}] = \frac{\delta F[n(\mathbf{r})]}{\delta n(\mathbf{r})} . \quad (7)$$

This potential includes both the Coulomb and the exchange-correlation potentials.

2 Finding the potential

In this section we wish to find a way to determine the individual charge densities $n_i(\mathbf{r})$. We begin by noting that if n_i is, as we assume, “v-representable”, then there is a one-to-one correspondence between the density n_i and a potential v_i , such that the wave functions described in (2) and (3) satisfy the Schrödinger equation

$$-\nabla^2 \psi_{i\alpha}(\mathbf{r}) + v_i(\mathbf{r}) \psi_{i\alpha}(\mathbf{r}) = \epsilon_{i\alpha} \psi_{i\alpha}(\mathbf{r}) , \quad (8)$$

This is equivalent to rewriting the SCAD density Functional (1) in the form

$$E[\{v_i(r)\}] = \sum_i T_0[v_i(r)] + \left\{ T_{TF}[n(\mathbf{r})] - \sum_i T_{TF}[n_i(\mathbf{r})] \right\} + F[n(\mathbf{r})] . \quad (9)$$

Now consider changing the potential in (9)

$$v_i(\mathbf{r}) \rightarrow v_i(\mathbf{r}) + \delta v_i(\mathbf{r}) . \quad (10)$$

This change in the potential at the site i changes the associated wave functions

$$\psi_{i\alpha}(\mathbf{r}) \rightarrow \psi_{i\alpha}(\mathbf{r}) + \delta\psi_{i\alpha}(\mathbf{r}) , \quad (11)$$

where, to first order in δv_i ,

$$[\epsilon_{i\alpha} + \nabla^2 - v_i(\mathbf{r})]\delta\psi_{i\alpha}(\mathbf{r}) = (\delta v_i(r) - \delta\epsilon_{i\alpha})\psi_{i\alpha}(\mathbf{r}) . \quad (12)$$

Without loss of generality we may take each $\delta\psi$ to be orthogonal to the corresponding ψ :

$$\int \delta\psi_{i\alpha}^*(\mathbf{r}) \psi_{i\alpha}(\mathbf{r}) d^3r = 0. \quad (13)$$

Multiplying both sides of (12) by $\psi_{i\alpha}^*(\mathbf{r})$ and integrating, we obtain the first order change in the eigenvalue:

$$\delta\epsilon_{i\alpha} = \int |\psi_{i\alpha}(\mathbf{r})|^2 \delta v_i(\mathbf{r}) d^3r . \quad (14)$$

The electron density on site i then changes by an amount

$$\delta n_i(\mathbf{r}) = 2\Re \sum_{\alpha} \delta\psi_{i\alpha}^*(\mathbf{r}) \psi_{i\alpha}(\mathbf{r}) , \quad (15)$$

which is a change of $O[\delta v_i]$. ($\Re z$ is the real part of z .) Note that the densities n_j on the other sites will not change, since by supposition we are only changing the spherical potential on site i , and there is no charge transfer. Thus

$$\delta n(\mathbf{r}) = \delta n_i(\mathbf{r} + \mathbf{R}_i) . \quad (16)$$

The kinetic energy T_0 (2) changes by an amount

$$\delta T_0 = -2\Re \sum_{\alpha} \int \delta\psi_{i\alpha}^*(\mathbf{r}) \nabla^2 \psi_{i\alpha}(\mathbf{r}) d^3r . \quad (17)$$

By (8) this becomes

$$\delta T_0 = 2\Re \sum_{\alpha} \int \delta\psi_{i\alpha}(\mathbf{r}) [\epsilon_{i\alpha} - v_i(\mathbf{r})] \psi_{i\alpha}(\mathbf{r}) d^3r . \quad (18)$$

Applying (13) and (15), we find

$$\delta T_0 = - \int v_i(\mathbf{r}) \delta n_i(\mathbf{r}) . \quad (19)$$

The other parts of the density functional change in a straight-forward way:

$$\delta F[n(\mathbf{r})] = \int v_{KS}[n(\mathbf{r}); \mathbf{r}] \delta n_i(\mathbf{r}) d^3r , \quad (20)$$

$$\delta T_{TF}[n(\mathbf{r})] = \int v_{TF}[n(\mathbf{r}); \mathbf{r}] \delta n_i(\mathbf{r}) d^3r , \quad (21)$$

and

$$\delta T_{TF}[n_i(\mathbf{r})] = \int v_{TF}[n(\mathbf{r}); \mathbf{r}] \delta n_i(\mathbf{r}) d^3r , \quad (22)$$

where

$$v_{TF}[n(\mathbf{r}), \mathbf{r}] = \frac{\delta T_{TF}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = (3\pi^2)^{\frac{2}{3}} n^{\frac{2}{3}}(\mathbf{r}) \quad (23)$$

is the Thomas-Fermi potential.

Substituting equations (19-23) into the energy formula (9), we find that it changes by an amount

$$\delta E[\{v_i(r)\}] = \int \{v_{KS}[n(\mathbf{r}); \mathbf{r}] + v_{TF}[n(\mathbf{r}); \mathbf{r}] - v_{TF}[n_i(\mathbf{r}); \mathbf{r}] - v_i(\mathbf{r})\} \delta n_i(\mathbf{r}) d^3r . \quad (24)$$

Equation (24) must hold for an arbitrary infinitesimal change in the potential δv_i . By (15) and (12), this produces a corresponding change in δn_i . Hence (24) must hold for arbitrary infinitesimal changes in δn_i , which can only occur if the term in curly brackets vanishes, i.e., if

$$v_i(\mathbf{r}) = v_{KS}[n(\mathbf{r}); \mathbf{r}] + v_{TF}[n(\mathbf{r}); \mathbf{r}] - v_{TF}[n_i(\mathbf{r}); \mathbf{r}] . \quad (25)$$

3 Spherical Averages

When using the SCAD model for crystals with atoms at high symmetry sites, it is often useful to assume that the densities n_i are spherically symmetric. This can be achieved by assuming that the n_i represent a closed shell system, and that each potential v_i is spherical. Under these assumptions, the formalism developed in Section 2 remains the same until equation (24), except that we replace the arbitrary potential $v_i(\mathbf{r})$ by the spherical potential $v_i(r)$, and restrict the potential changes to the spherical $\delta v_i(r)$. At that point we note that because of the assumption that n_i represents a closed shell, $\delta n_i(\mathbf{r})$ must also be spherical. Thus (24) can be written

$$\delta E[\{v_i(r)\}] = \int \{v_{KS}[n(\mathbf{r}); \mathbf{r}] + v_{TF}[n(\mathbf{r}); \mathbf{r}] - v_{TF}[n_i(\mathbf{r}); \mathbf{r}] - v_i(r)\} \delta n_i(r) d^3r . \quad (26)$$

This holds for arbitrary spherical potential changes $\delta v_i(r)$, whence $v_i(r)$ must obey

$$v_i(r) = \frac{1}{4\pi} \int \{v_{KS}[n(\mathbf{r}); \mathbf{r}] + v_{TF}[n(\mathbf{r}); \mathbf{r}] - v_{TF}[n_i(\mathbf{r}); \mathbf{r}]\} d\Omega , \quad (27)$$

where the integral is over the surface of a sphere of radius r . Note that this is just the spherical average of the full potential (25):

$$v_i(r) = \frac{1}{4\pi} \int v_i(\mathbf{r}) d\Omega . \quad (28)$$

4 Discussion

The essential difference between the SCAD model and the more familiar Kohn-Sham LDA formulation is that the SCAD model approximates kinetic energy in low-density regions (outside atomic cores) with the aid of a local functional. While the total density in the SCAD model is expressed as a sum of localized densities, this should not be a major source of error, provided that the localized densities are given adequate flexibility. Solving the atomic calculations self consistently, with the potential for each site determined from the densities and potentials of the rest of the system, puts the atomic energy levels on a common scale. Just as in the Kohn-Sham treatment, the lowest energy levels are occupied to achieve the minimum total energy.

The SCAD model offers some advantages over the Kohn-Sham LDA approach. It is generally more efficient, particularly for large systems, because the computational labor increases linearly with the number of atoms in the system. Moreover, it is ideally suited for application on a massively parallel computer. Finally, we note that the SCAD model has the correct behavior in the limit of infinitely separated atoms, whereas, each electron in the Kohn-Sham model is delocalized and remains so in this limit.

5 Acknowledgment

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References

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